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ADDITION AND INSERTION REACTIONS OF PHENYLNITRENOID WITH AROMATIC SUBSTRATES. SYNTHESIS OF 1-PHENYL-1*H*-AZEPINE

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Phenylnitrene generated photolytically or thermally from phenyl azide fails to add to benzene[1], although intramolecular additions[2] and cyclizations[3] are well known. Intermolecular substitutions of reactive aromatic substrates such as mesitylene and N,N-dimethylaniline have been observed with more electrophilic arylnitrenes specifically p-cyanophenylnitrene[4], p-nitrophenylnitrene[4], p-trifluoromethylphenylnitrene[4], and 2-pyrimidylnitrene[5]. We now wish to report an example of the formal addition of phenylnitrene to benzene to give 1-phenyl-1*H*-azepine which presumably proceeds via a nitrenoid mechanism.

Deoxygenation of nitrosobenzene by triethyl phosphite in benzene-trifluoroethanol as solvent gives β,β,β-trifluoro-*p*-phenetidine (21%), N-ethyl-β,β,β-trifluoro-*p*-phenetidine and an orange solid mp 49-49.5° (34%) having the empirical formula $C_{12}H_{11}N$. The latter compound is identified as 1-phenyl-1*H*-azepine on the basis of the following data. The nmr spectrum depicted in Figure 1 shows 6 nonaromatic protons showing a coupling and chemical shift pattern very similar to that of 1-carbethoxy-1*H*-azepine.[3] The ultraviolet spectrum in 95% ethanol, λ_{max} 280mμ(ϵ = 16,000), confirms a nonbenzenoid chromophore. The compound is hydrogenated to 1-phenylhexahydro-1*H*-azepine identified by spectral and mp data: hydrochloride, 193-193.5° (lit.[7] mp 194°); hydrobromide, 217-219° (lit.[7] mp 219°). 1-Phenyl-1*H*-azepine is rearranged to diphenylamine by dilute acid.

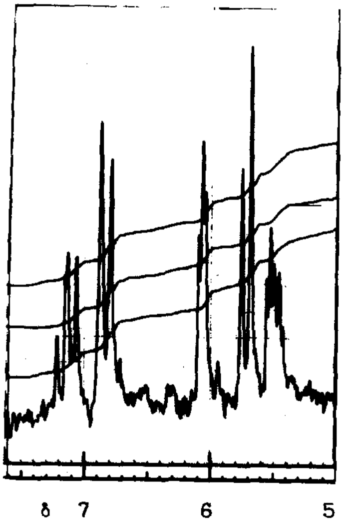
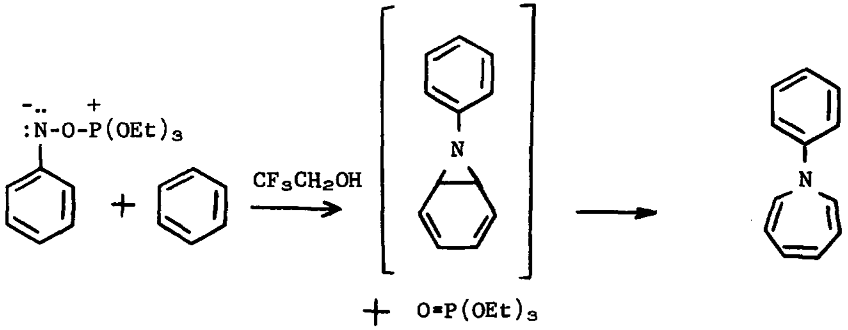


Figure 1. 100 MHz NMR Spectrum of 1-Phenyl-1H-azepine in CCl_4.

Similar deoxygenation of nitrosobenzene in xylene-trifluoroethanol followed by chromatography of the reaction product gave 2,5-dimethyldiphenylamine, mp 29° (9 %) and 4-methyl-N-phenylbenzylamine, mp 45° (6 %). The former compound was identified by its nmr spectrum, analysis and its ultraviolet spectrum which is very similar to that of diphenylamine. The latter compound is known (lit.[8] mp 47°) and its nmr spectrum in carbon tetrachloride shows a single methyl peak (2.38δ) and a methylene signal (4.15 δ). GLPC analysis also indicated the formation of β,β,β-trifluorophenetidine (3%). Deoxygenation of nitrosobenzene in mesitylene-trifluoroethanol gave β,β,β-trifluorophenetidine (17%) and 2,4,6-trimethyldiphenylamine (57%). A minor basic component ($<$ 5%) which was isolated by preparative thin layer chromatography has spectral properties in accord with expectation for 3,5-dimethyl-N-phenylbenzylamine and was characterized as a hydrochloride, mp 170°-171°.

Trifluoroethanol is unique among the alcohols investigated in promoting nitrenoid additions to benzene. Deoxygenation in methanol, ethanol, isopropanol, t-butanol and β,β,β-trichloroethanol gave only o- and p-alkoxyanilines[9].

Attempts to observe addition of phenylnitrene from phenyl azide to benzene in the presence of trifluoroethanol indicate that trifluoroethanol has no more than a marginal effect on the reactivity of phenylnitrene generated photolytically. At most only traces of diphenylamine or 1-phenyl-1H-azepine were detectable by glpc after photolysis of phenyl azide to 40% completion in trifluoroethanol-benzene. However, 1-phenyl-1H-azepine is not stable to the photolysis conditions. Similar photolyses in the presence of trifluoroacetic acid added to promote rearrangement to the photochemically stable diphenylamine give diphenylamine in 0.5% yield as measured gas chromatographically and identified by infrared spectroscopy after isolation by preparative thin layer chromatography. At present, therefore, we attribute the observed reactions to the nitrenoid species generated as the first intermediate in the deoxygenation process[9]. Speculation on the mechanism by which trifluoroethanol enhances the nitrene-like reactivity of the intermediate is deferred until more extensive data are available.



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